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(54) **High yield pulping process.**

(57) There is disclosed a high yield pulping process comprising impregnating chips with an alkaline peroxide solution containing stabilizers for peroxide followed by mechanical defibration, in which the wood chips are pretreated prior to peroxide impregnation, said pretreatment comprising:

- (a) impregnating the chips with an impregnation solution consisting essentially of a chelating agent for metallic ions; and,
- (b) expressing from the chips chelating agents and metallic ions.

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Pulping processes can be put into either of two broad classifications; high yield pulping and chemical pulping. High yield pulping processes use mechanical destructuring (i.e. grinding, refining) of the raw material to produce individual fibers or pulp from lignocellulosic materials, usually in chip form, sometimes with mild chemical pretreatment of the chips. Chemical pulping or low yield processes that primarily use chemical reactions to produce individual fibers from chips. Within the high yield category there are many different combinations of mechanical, chemical, and thermal treatments. Each specific combination of mechanical, chemical and thermal treatments has a different effect on fiber separation, lignin removal, fiber brightness and papermaking strength of paper made from the resulting fibers.

This invention concerns high yield pulping comprising chemical pretreatments using peroxide in combination with mechanical treatment to produce pulp from chips. More particularly, this invention reduces peroxide decomposition associated with the pretreatment of chips with peroxide prior to refining of the chips to produce high yield pulp with peroxide modification of the lignin in the fibers. With this invention pulp having desired papermaking properties, particularly a combination of high strength and brightness is obtained with reduced chemical and energy consumption.

Pulp produced by mechanical refining alone without chemical pretreatment results in extremely high yields (about 95% or higher) but results in fibers containing almost all of the original lignin in essentially a chemically unmodified form and fiber damage/fines generation due to the somewhat indiscriminate mechanical action on the lignocellulosic raw material. Such unmodified lignin imparts relatively low brightness to the fibers, and, due to its hydrophobic nature, the lignin inhibits the development of paper strength through fiber collapse and fiber to fiber bonding (hydrogen bonding). Such fibers are stiffer than partially or completely delignified fibers from the same lignocellulosic raw material. Although some high yield pulps containing high amounts of lignin can be bleached economically to relatively high brightnesses using oxidizing agents such as alkaline peroxide, and/or reducing agents such as sodium hydrosulfite, such post-refining treatments do not increase papermaking strength to levels required for many end uses because much irreversible mechanical damage and fines generation has already been done to the fibers in the refining process. Chemically attacking the lignin before refining prevents much of the mechanical damage and fine generation. Such chemical pretreatment with peroxide prior to refining is improved by the present invention.

The papermaking strength of high yield pulps can be increased by sulfonation of the lignin, particularly when the wood chips are treated with the sulfonation chemicals (usually sodium sulfite with or without sodium hydroxide) prior to mechanical defibration (refining). In some cases, the resulting fibers can also be bleached economically as with alkaline peroxide and/or sodium hydrosulfite to give both improved brightness and papermaking strength. However, the higher levels of sulfonation required for high strength result in pulps which respond less well to bleaching than similar non-sulfonated or low-sulfonated pulps, and therefore such highly sulfonated pulps have high strength but have lower bleached brightnesses and higher bleach chemical demand. Conversely, low-sulfonation pulps are more bleachable but have lower strength. Moreover, sulfonation processes require the removal and disposal of environmentally objectionable sulfur compounds from process waste streams. In addition, the need for separate sulfonation, refining, and post-refiner bleaching equipment makes the capital equipment and operating costs for such a system very significant.

An alternative to sulfonation of lignin for increasing papermaking strength of high yield fibers is carboxylation and brightening of lignin achieved by the combined swelling and brightening action of alkaline peroxide prior to and/or during defibration. As sulfonation results in lignin containing sulfonate groups, likewise, carboxylation results in lignin with carboxylate groups. Both the sulfonate and the carboxylate groups are capable of participating in hydrogen bonding which increases the strength of paper made from such high yield pulps (papermaking strength).

Similar to the alkaline high sulfonation treatment of chips prior to refining, alkaline peroxide pretreatment of chips softens the lignocellulosic raw material resulting in easier fiber separation (less energy consumption and less fines generation and fiber fragmentation) during refining. In addition, refiner brightening with alkaline peroxide can eliminate the need for separate post-refiner bleaching equipment, due to the facts that refiners are excellent mixers of pulp and brightening agents, and the temperature within the refiner (about 100°C or higher) causes brightening to occur extremely fast relative to typical post-refiner alkaline peroxide bleaching steps (approximately 50°C to 80°C). The primary drawback to brightening chips within the refiner with alkaline peroxide is peroxide decomposition. Peroxide decomposes to form oxygen (ineffective for lignin-retaining bleaching) and water under the highly alkaline conditions required for papermaking strength development. Peroxide decomposition is hastened by the high temperatures reached in refiners and by metal contaminants, particularly manganese, iron, and copper, which are contained in significant quantities in lignocellulosic raw materials and in lesser quantities in process water. Partial removal or

inactivation of such metal contaminants in lignocellulosic raw material can be effected by introducing chelating agents into the wood chips and then removing the chelant-metal complexes. However, the physical entrapment and chemical attraction of such metals by fiber components within the chips make complete removal of the metals impractical and require additional peroxide protection.

5 The problems associated with pre-refiner or in-refiner alkaline peroxide treatments are partially avoided by conventional post refiner alkaline peroxide treatments. For example, rather than removing metal contaminants from chips, the contaminants have been removed from individual fibers with chelating agents after refining and prior to alkaline peroxide bleaching. Post refining removal is much more easily achieved because the particle size of the fiber in pulp is much smaller than the size of chips before refining. The  
10 smaller size makes the metal contaminants much more accessible to the chelant solution. Consequently, in many cases the individual fibers can be bleached to much higher brightnesses with alkaline peroxide in a post refiner bleaching treatment without significant waste of peroxide bleaching agents due to metal contaminant induced decomposition of peroxide (U.S. Patent No. 4,160,693-Lindahl, et al.). The disadvantage is, that high strength requires high levels of pre-refiner sulfonation and high sulfonation makes post-refiner bleaching difficult.

15 There have been many attempts to overcome such problems associated with the pre-refiner or in-refiner use of alkaline peroxide in the production of high yield pulps. Control of alkalinity (e.g., see U.S. Patents 3,069,309-Fennell and 4,270,976-Sandstorm, et al., and Canadian Patents 1,078,558 and 1,173,604), control of the temperature (e.g., U.S. Patent 4,187,141-Ahrel), and control of time at high  
20 temperature (e.g., U.S. Patent 4,270,976-Sandstorm et al.) have been tried. However, such techniques for reducing peroxide decomposition also reduce the effectiveness of alkaline peroxide in terms of the resulting pulp properties (papermaking strength) while the presence of deleterious metal contaminants still results in inefficient utilization of the peroxide bleaching agent during refiner bleaching.

A common method for circumventing the problem of peroxide decomposition in alkaline peroxide  
25 bleaching of chips during refining is to add the bleaching agent directly to the refining zone to minimize the contact time between the chip and alkaline peroxide, and in some cases to allow more intimate contact between metal contaminants and silicate and/or magnesium ion stabilizer flocs (See for example, U.S. Patent Non. 3,023,140-Textor, 3,069,309-Fennell, 4,022,965-Coheen, et al., 4,270,976-Sandstorm, et al., 4,311,553-Akerlund, et al., Japanese Patent Application No. 80-72091, and Federal Republic of Germany  
30 Patent No. 2818-320). Additionally, wood chips have been pretreated by impregnation and/or refining with chelants (U.S. Patents Nos. 3,023,140-Textor, 4,311,553-Akerlund, et al., Japanese Patent Application No. 80-7209, and Federal Republic of Germany Patent No. 2818-320) or with sodium silicate (U.S. Patent Nos. 3,069,309-Fennell, 4,311,553-Akerlund, et al.), or with magnesium salts (U.S. Patent Nos. 3,023,140-Textor, 3,069,309-Fennell, 4,311,553-Akerlund, et al., and Japanese Patent Application 80-72091) and combinations  
35 thereof prior to alkaline peroxide addition into the refiner to reduce peroxide decomposition. U.S. Patent No. 4,270,076-Sandstorm, et al., is the only case in which brightness comparable to post refiner alkaline peroxide bleaching was obtained but it utilized lower alkalinity as the means of reducing the peroxide decomposition rate which sacrificed good papermaking strength development.

The present invention is based in part upon the hypothesis that with processes employing alkaline  
40 peroxide addition directly into the refiner, the majority of the defibration occurs before the alkali and peroxide can react with the wood fibers, thereby reducing the potential for papermaking strength development imparted with requiring more energy for refining and increasing the generation of fines, all of which could be avoided if alkaline peroxide could be inserted into and stabilized within the chip and allowed to react with the chip prior to defibration.

45 Impregnation of chips with alkaline peroxide prior to refining has also been practiced (U.S. Patents 4,187,141-Ahrel, and 4,270,976-Sandstorm, et al., and Canadian Patents 1,078,558, and 1,173,604). In most cases, the brightness obtained was comparable to that obtainable with post refiner alkaline peroxide bleaching. However, with such processes, metal contaminants are not removed or deactivated; rather, peroxide decomposition is reduced by lower alkalinity (U.S. Patent Nos. 4,270,976-Sandstorm, et al.,  
50 Canadian Patent 1,070,558, and 1,173,604) or by minimizing refining temperature (U.S. Patent No. 4,187,141-Ahrel). However, the lowering of the alkalinity or temperature causes less papermaking strength to be developed than with high sulfonation methods. Lowering of the temperature below 100 °C is difficult to accomplish practically. At higher alkalinity, strengths comparable to those of post refiner bleached, sulfonated high yield pulps were obtained but at the expense of lower brightness due to increased peroxide  
55 decomposition (Canadian Patent No. 1,078,558).

Additional examples of prior art teachings of treating pulp (rather than chips) with peroxide demonstrate the continuing tendency in the art to avoid treating chips with peroxide because of the decomposition problem. U.S. Patent No. 4,787,959 is another example of a high yield pulping process that avoids peroxide

treatment of chips by treating pulp rather than chips with peroxide using a first alkaline cooking stage to fiberize the chips prior to a second cooking with peroxide. By the time the peroxide is added in this process the "lignin-cellulose" material exists as more or less discrete fibers because the cellular structure has been fractured. Thus, the problem of peroxide stability within the cells of chips or wood particles does not exist.

5 Thus in many recent prior art patents such as, U.S. Patents 4,787,959, 4,734,161 and 4,732,650 the material being treated is pulp made up of small fibers, so the problem of stability of peroxide within the essentially unbroken cellular structure of wood particles existing prior to the refining does not exist.

Alkaline peroxide stabilizers like water soluble alkaline sodium silicate and magnesium sulfate are often utilized in the peroxide bleaching of high yield pulps to further reduce peroxide decomposition caused by 10 metal contaminants. The silicate-magnesium combination forms a floc in alkaline peroxide solutions and this floc attracts and absorbs the metal ions thereby reducing the ability of such ions to decompose peroxide. Magnesium ions also reduce peroxide decomposition by electronically deactivating the metal ions, thereby reducing the potential of the metal ions to decompose peroxide.

Recently, it was discovered that flocs or precipitates formed by silicates and/or magnesium in alkaline 15 peroxide solutions cannot readily penetrate into the wood chip structures prior to refining due to the physical size of the flocs relative to the pore size of the wood chips. The discovery was based upon the observation that such stabilizers effectively stabilize peroxide against decomposition when pulp is being bleached with peroxide but are not as effective when the same fibers are still in chip form rather than pulp. It was postulated that the difference in stabilizer effectiveness when treating pulp fibers versus wood chips 20 is due to the relatively small molecules of alkali and peroxide entering the cellular structure of the chip while the stabilizer floc is impeded from penetrating into the cells to counteract decomposition induced by metal contaminants within the cellular structure. The alkaline peroxide in the chips, upon entering the cellular structure and becoming separated from the stabilizing floc, rapidly decomposes thereby reducing the amount of peroxide available for bleaching during refining. In addition, the pressure buildup within the chip 25 due to the evolution of oxygen gas during peroxide decomposition forces alkaline peroxide solution back out of the chip resulting in insufficient peroxide retention in the chip as it enters the refining zone. Furthermore, irreversible alkaline yellowing of the pulp occurs if there is insufficient residual peroxide remaining with the pulp after refining.

U.S. Patent 4,849,053 to Gentile, et al. and the references cited during the prosecution of that patent 30 are the most pertinent prior art, over which the present invention constitutes an improvement. The Gentile, et al. patent describes and claims a highly successful method for producing wood pulp from chips using pre-treatment with stabilizers and alkaline peroxide prior to mechanical fiberization (refining) to increase the brightness of the resulting fibers and papermaking strength achievable with the fibers. This sequential pre-treatment of the wood chips prior to refining results in the "in-situ" formation within the chips of a peroxide- 35 stabilizing floc or sol.

The alkaline peroxide impregnated chips with the "in-situ" formed stabilizing floc within the cellular structure are refined in one or more stage(s) under atmospheric pressure or superatmospheric pressure and the corresponding saturated steam temperature. (The refining pressure is usually associated with steam added to or generated within the refining device.) The resulting pulp is dewatered and washed to remove 40 bleaching and stabilizing chemicals and dissolved wood substances to result in a non-sulfonated pulp having a unique combination of properties including high yield, superior brightness and papermaking strength, and low fines content. Recyclable alkaline peroxide is obtained from the dewatering of the pulp after refining and preferably before acidification. The alkaline peroxide obtained from the post refiner dewatering step can be reused as makeup in the impregnation step in which peroxide is added to the chips.

45 The two or three stage impregnation and pulping process of Gentile et al. (U.S. Patent 4,849,063) is designed to stabilize alkaline peroxide so it can effectively and economically develop pulp strength and brightness by the time the pulp exists the mechanical pulping stage (refiner). This method, while eminently successful on most species of wood chips, does not produce the maximum stabilization of alkaline peroxide. For example, with wood chips from such softwoods as eastern black spruce, eastern balsam fir, 50 lodgepole pine/white spruce (50/50% mix), and hardwoods such as aspen, the peroxide is not stabilized as completely as possible in the normal fashion, some peroxide decomposition occurs and maximum brightness is not achieved as economically as possible with the practice of the present invention.

#### SUMMARY OF INVENTION

55 The present invention is based upon the discovery that the key to the realization of successful peroxide stabilization and brightening utilization lies in (1) substantial reduction of metallic ions content in the chips, such as iron, copper, and (in particular) manganese content in the chips (these metals catalyze peroxide

decomposition) prior to impregnation of chips with peroxide and (2) the maintenance of high level of magnesium in the chips with the alkaline peroxide prior to and preferably during refining.

The present invention provides an alkaline peroxide process for the production of high yield pulps from wood chips having a reduced manganese concentration prior to peroxide impregnation and increased  
 5 magnesium concentration prior to or simultaneously with alkaline peroxide impregnation, followed by refining to produce a pulp of high brightness and pulp strength with a minimum of peroxide consumption.

#### DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

10 This invention is directed toward the removal of metallic ions such as manganese from lignocellulosic material in chips form prior to treatment with alkaline peroxide and to the utilization of high levels of magnesium (Mg) within the chips while in contact with alkaline peroxide. The present invention is particularly useful for pulps from wood species naturally high in metallic ions such as eastern black spruce, eastern balsam fir, lodgepole pine/white spruce mixtures and aspen.

15 The present process is characterized by at least a two stage and preferably three or more stage impregnation process of chips prior to refining. In the first stage, wood chips, which preferably have been purged of entrapped air, are impregnated with a chelating agent such as diethylenetriaminepentaacetic acid (DTPA), ethylene diaminetetraacetic acid (EDTA), hydroxyethylethylenediamine triacetic acid (HEEDTA), and nitrilotriacetic acid (NTA), sodium tripolyphosphate (STPP), and phosphonic acid derivatives or other  
 20 similar compounds known in the art for such functionality or a combination of such chelating agents. The concentration of the chelating agent in the impregnating solution should be preferably from 0.1 gram/liter to 20 grams/liter (expressed as 100% chelating agent in the solution) to give preferably 0.01% to 2% chelant based on the dry weight of the chips with from 0.05% to 0.5% being particularly preferred. The temperature of the first impregnation step is preferably between 15°C and 80°C. The pH is preferably between 4 and  
 25 12 with between 8 to 11 being particularly preferred. Adjustments to the solution pH can be made with any suitable acid or alkaline substance which does not react with peroxide, cause darkening of the chips, or cause any of the components of the impregnation solution to be precipitated or to lose chelating ability such as sulfuric acid or sodium hydroxide.

Before, or as part of the first impregnating step, the chips are preferably squeezed to expel liquid and  
 30 any remaining air and then allowed to expand in contact with the impregnation solution. The quantity of solution absorbed in an impregnation step is influenced by the impregnation device (primarily the degree of squeezing of the chips) and the particular material being impregnated. The level of chemical addition into the chips is primarily controlled by the concentration of the particular chemical in the impregnating solution and the quantity of solution absorbed. The concentration of chelant and quantity of solution absorbed is  
 35 preferably adjusted to give a chemical addition of 0.01% to 2% based on the dry weight of lignocellulosic material being treated. The first impregnation solution is expressed either prior to or as the initial part of the second impregnation step. Metallic ions are removed from the chips with the expressed first impregnation solution which removal is enhanced by the presence of the chelating agents. Preferably at least about 25% of the first impregnation solution is expressed from the chips with from about 33% to about 50% being  
 40 particularly preferred. The effectiveness of the first impregnation step to remove metallic ions is enhanced by providing some retention time between impregnation and expressing the impregnation solution from the chips. This enhanced effectiveness is observed with a retention time of one half hour although several hours is more effective. Since the first impregnation stage is primarily for the purpose of removing metallic ions from the chips, the first impregnation solution should consist essentially of a chelating agent because it is  
 45 expressed from the chips. The presence of substantial quantities of peroxide (e.g. above 1%) or stabilizers in the first impregnation solution would be wasteful of such chemicals since they would be removed from the chips when the first impregnation solutions is expressed from the chips. Metallic stabilizers, particularly magnesium should be avoided in the first stage because they interfere with the primary purpose of the chelating agent.

50 The second impregnation step can be a conventional alkaline peroxide impregnation stage with stabilizers and chelating agents. Preferably the second impregnation stage is with an aqueous solution of soluble magnesium salts (e.g., epsom salt -  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ). The epsom salt addition level is 0.05% to 2% based on oven dried (o.d.) wood expressed as  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ . This can be readily accomplished with an impregnation solution containing 0.5 grams per liter to 20 grams per liter. The purpose of this second step  
 55 is to allow the soluble magnesium salts to penetrate the chip interstices. The temperature of the second impregnation step is preferably between 15°C and 80°C, and the pH is maintained below 10 to keep the magnesium in a soluble form. Adjustment to the solution pH is preferably made in the same manner as described for the first impregnation solution. Optionally, the second impregnation solution can contain

alkaline peroxide with silicate stabilizers.

The third impregnation solution is an aqueous alkaline peroxide solution which contains peroxide stabilizers such as silicates. Preferably the third impregnation solution contains magnesium and silicate stabilizers. Silicates are preferably in a concentration range of 1 gram per liter to 50 grains per liter to yield  
 5 between 0.1% to 5% by weight of silicates (calculated as  $\text{SiO}_2$ ) based upon the dry weight of the chips. Magnesium based on weight of Mg in salt, is preferably in a concentration of from 0.01 grams per liter to 2 grams per liter to result after impregnation in from 0.001% to 0.2% by weight Mg based upon the dry weight of the chips. The third impregnation solution contains preferably hydrogen peroxide although any other peroxygen compound suitable for lignin brightening may be used. The peroxygen compound is  
 10 preferably in the concentration range of between 5% and 100 grams per liter (calculated and expressed as hydrogen peroxide) to give additional levels of preferably between 0.5% and 10% of the dry weight of chips expressed as hydrogen peroxide. In addition, an alkaline substance (preferably sodium hydroxide) is added to the third impregnation solution to give a solution pH preferably in the range between 9 and 13 with between 10 and 12.5 being most preferred.

15 The most preferred impregnation sequence is the three stage sequence previously described and presented in greater detail in the examples. However, it should be understood that the invention is not limited to the generally described three stage sequence. A two-stage impregnation sequence in which the first impregnation stage is practiced as previously described and the second impregnation (Mg compounds) solution is combined with the third impregnation solution (alkaline peroxide and peroxide stabilizers such as  
 20 silicates) and used as the impregnation solution in the second stage, preferably at a pH from 9 to 13 can also be employed.

It is important that the entire chip become uniformly impregnated with any reactant solutions. Best results are achieved when a squeezing ratio (equal to mass of liquid squeezed from the chips per unit mass of dry chips) of unity or slightly higher is achieved. This requires a compression ratio of about 4:1, and  
 25 results in the chips being squeezed from about 33% solid to about 50% solids. In other words, about 50% of the liquid present in the chips entering the compression device is squeezed out and replaced by "new" liquid in the impregnation expansion which follows.

The invention is not limited to the concentration and addition level ranges previously described for stabilizers and chelating agents, since differences in metal contamination levels of lignocellulosic raw  
 30 materials or process water could justify stabilizer or chelating agent usages outside of the specified preferred ranges.

Optionally, the chemically treated chips can be allowed to react with or without the application of heat, prior to entering the refining stage by retaining the impregnated chips for some finite time in any suitable vessel. A retention time of 5 minutes to 60 minutes is particularly suitable. Each impregnation is preferably  
 35 followed by a short drainage period and additional time for diffusion and/or reaction to occur within the chips. The amount of diffusion/reaction time required depends on the type of wood processed.

#### Refining of Chemically Impregnated Chips (Defibration)

40 The chemically treated chips are mechanically refined in a suitable defibration apparatus in one or more stages in accordance with conventional processes and equipment. The steam pressure and corresponding temperature during refining are optional and can be at atmospheric and/or superatmospheric pressure, depending on the species being pulped and the desired pulp properties. Atmospheric pressure refining is preferred.

45 After refining, it is preferred that the pulp remain alkaline so that the silicate and other pH-sensitive materials can be removed prior to washing and neutralization. This prevents silicate deposition which can impair final pulp properties.

#### Post-Refining Steps:

50 After refining, the pulp may be allowed to continue bleaching as long as is practical prior to expelling the impregnation solutions. The amount of peroxide used in the impregnation steps is preferably preselected to result in some residual peroxide remaining after refining in order to maintain high brightness. Preferably the refined pulp is concentrated, e.g., by compressing or thickening, to remove residual  
 55 impregnation solution containing potentially recyclable alkaline peroxide, then diluted with water, washed and acidified preferably with sulfur dioxide, sodium bisulfite, sulfurous acid, or sulfuric acid, to a pH between 5.5 and 6.0. In particular, washing prior to acidification is preferred for removal of alkali soluble wood components and silicate. The residual peroxide extracted from the pulp after refining can be recycled

as a source of peroxide in one of the impregnation solutions particularly if the process is practiced continuously or in sequential batches. The washed pulp is preferably screened and cleaned by conventional means to result in a pulp suitable for the production of paper products.

## 5 EXAMPLES

In the following examples wood chips from eastern black spruce, eastern balsam fir, lodgepole pine/white spruce 50/50 mixture (all softwoods) and/or aspen (hardwood), are treated by both the process of the present invention and that of Gentile, et al., U.S. Patent 4,849,058 and a comparison of the results  
10 tabulated. The process of U.S. Patent 4,849,058 was chosen for comparison because it represents the what is believed to be the best of the prior art processes for stabilizing alkaline peroxide in chips prior to high yield mechanical pulping. In the examples, all parts are by weight unless specified otherwise.

### EXAMPLES A (CONTROL) AND 1

15

Screened eastern black spruce chips (2000 grams o.d. of wood at a solid content of 49%) were steamed for 15 minutes. The hot chips (solid content 40%) were placed into a Sprout-Bauer L1-12 laboratory impregnator and compressed to a solids content of 60-70%. The impregnator was then closed, filled with 55 liters of impregnation liquor and the chips released (allowed to expand) into the liquor. The  
20 impregnated chips were removed from the impregnator and drained for 5 minutes to remove all excess liquor. The same procedure was repeated for all three impregnation stages. In Example A, the preferred three-stage impregnation process of U.S. Patent 4,849,058 was employed. In Example 1, the 3 impregnation steps were conducted according to the process of the present invention.

Table 1 lists the impregnation conditions, the amount and type of chemicals added, and the test results  
25 comparing the process of the present invention (Example 1) with the control (Example A).

The amounts of chemicals applied during impregnation were determined as follows:

Ca = (0.1) (PUR)(CL), where  
Ca = amount of chemical applied in % by weight of oven dried (o.d.) wood  
CL = concentration of chemicals in liquor in grams/liter  
30 PUR = amount of liquor picked up during impregnation in liters divided by oven dried (o.d.) weight of wood in kilograms (kg)

The magnesium salt used in these examples was Epsom salt ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ). The reported amounts of pentasodium salt of diethylenetriamine-pentaacetic-acid (DTPA) are based on a solution with 40.2% active ingredient. Trisodium salt of hydroxy-ethylethylene-diamine-triacetate (HEEDTA) was a 41.3% solution.  
35 Also, the concentrations for silicate are calculated using a 37.6% solution with a  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio of 3.22.

After impregnation chips were refined in a Sprout-Bauer 12-1CP laboratory refiner under atmospheric pressure. After refining residual peroxide and caustic were determined by titration. The pulp was dewatered, washed and the pH adjusted to 6.0 with dilute  $\text{H}_2\text{SO}_4$ . "Brightness" is defined as ISO brightness in percent units which is determined by using the sample preparation procedure given in the Technical Association of  
40 the Pulp and Paper Industry (TAPPI) Official Test Method T218 om-83. The brightness of the sample was measured using a Technibrite Micro TB-IC meter.

Hydrogen peroxide usage or consumption (expressed as a weight percent of the dry weight of the chips) is based on the quantity of peroxide applied to the wood chips minus the quantity of residual peroxide in the pulp after refining. The percentage peroxide consumed is calculated as being equal to the  
45 quantity of peroxide consumed times 100 divided by the dry weight of the chips. The quantity of peroxide in a solution was determined by iodometric titration using starch as an end point indicator (Vogel, Quantative Inorganic Analysis, Wiley & Sons, 1961, p. 363).

The magnesium and manganese concentration in the original wood chips and after impregnation was determined by atomic absorption spectroscopy.

50 As shown, the process of the present invention led to an increase in manganese removal and magnesium retention, which in turn gave a 2% brightness increase and a 47% reduction in peroxide consumption, thus demonstrating the increased peroxide stability under the process of the present invention.

55

TABLE I

Process conditions, added chemical amounts, test results of  
3-stage alkaline peroxide process of present invention vs  
control 3-stage process.

EXAMPLE NO.	A (CONTROL)		#1	
	EASTERN		EASTERN	
TYPE WOOD:	BLACK SPRUCE		BLACK SPRUCE	
1. 1st Impregnation,				
a. process conditions				
pH	7.0		11.0	
b. chemicals added				
CL		CA	CL	CA
DTPA	1.35	0.22	2.5	0.39
HEEDTA	1.35	0.22	2.5	0.39
MgSO <sub>4</sub> ·7H <sub>2</sub> O	3.35	0.53	-	-
2. 2nd Impregnation				
a. process conditions				
pH	10.8		9.5	
b. chemicals added				
DTPA	1.25	0.19	-	-
HEEDTA	1.25	0.19	-	-
Silicate	12.5	1.9	-	-
MgSO <sub>4</sub> ·7H <sub>2</sub> O	-	-	3.35	0.53
3. 3rd Impregnation				
a. process conditions				
pH	11.6		11.2	
b. chemicals added				
MgSO <sub>4</sub> ·7H <sub>2</sub> O	4.5	0.54	3.35	0.48
Silicate	16.5	2.13	26.65	3.81
NaOH	31.7	4.09	27.20	3.89
H <sub>2</sub> O <sub>2</sub>	33.5	4.32	27.20	3.89
4. Total Chemicals Added				
DTPA		0.41		0.39
HEEDTA		0.41		0.39
MgSO <sub>4</sub> ·7H <sub>2</sub> O		1.07		1.01
Silicate		4.03		3.81
NaOH		4.09		3.89
H <sub>2</sub> O <sub>2</sub>		4.32		3.89



## 5. Test Results

		CA	CA
	ISO brightness (%)	74.1	76.1
	H <sub>2</sub> O <sub>2</sub> consumed (%)	3.74	2.73
5	NaOH consumed (%)	3.35	3.18
	PUR 3rd stage (l/kg)	1.29	1.43
	Mn in chips		
	3rd stage (ppm)	10.3	8.4
	Mg in chips		
	3rd stage (ppm)	364	1050
10	Mn content original		
	chips (ppm)	37.5	37.5
	Mg content original		
	chips (ppm)	73.5	73.5

COMPARISON

15	<u>Control:</u>	74.1% brightness 3.74% H <sub>2</sub> O <sub>2</sub> consumption 10.3 ppm Mn in 3rd stage chips 364 ppm Mg in 3rd stage chips
20	<u>Invention:</u>	76.1% brightness 2.73% H <sub>2</sub> O <sub>2</sub> consumption 8.4 ppm Mn in 3rd stage chips 1050 ppm Mg in 3rd stage chips
25	<u>Improvement:</u>	2.0 greater brightness units 27% decrease in H <sub>2</sub> O <sub>2</sub> consumption 1.9 ppm less Mn in 3rd stage chips 686 ppm more Mg in 3rd stage chips

EXAMPLES B (CONTROL) AND 2

30 Two kilograms of screened eastern Canadian balsam fir chips with a solids content of 56.2% were impregnated and refined as in control Example A. The pH of the first stage liquor was adjusted to 7.0 and the 2nd stage liquor pH was 10.7. This experiment is designated as comparative Example B.

35 A three impregnation step sequence of the present invention was made on an identical batch eastern Canadian balsam fir chips as used in Example B. The general impregnation and refining conditions were the same as for Example 1 above. Table 2 lists the process conditions, chemical types and amounts added, and the comparative test results for both examples. This experiment is designated as Example 2.

40 As with Examples A and 1, the greater manganese removal from the chips and greater magnesium addition to the chips prior to refining gave improved brightness (1.5 ISO brightness units) and reduced (27%) peroxide consumption compared to the control.

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TABLE II

Process conditions, added chemical amounts, test results  
of 3-stage alkaline peroxide process of present invention  
vs. control 3-stage process.

EXAMPLE NO.	B (CONTROL)		#2	
TYPE WOOD:	EASTERN		EASTERN	
	BALSAM FIR		BALSAM FIR	
1. 1st Impregnation				
a. process conditions				
pH	7.0		11.0	
b. chemicals added	CL	CA	CL	CA
DTPA	1.70	0.24	3.35	0.49
HEEDTA	1.70	0.24	3.35	0.49
MgSO <sub>4</sub> ·7H <sub>2</sub> O	4.45	0.64	-	-
2. 2nd Impregnation				
a. process conditions				
pH	10.7		9.5	
b. chemicals added				
DTPA	1.90	0.27	-	-
HEEDTA	1.90	0.27	-	-
Silicate	18.85	2.71	-	-
MgSO <sub>4</sub> ·7H <sub>2</sub> O	-	-	5.0	0.65
3. 3rd Impregnation				
a. process conditions				
pH	11.3		11.0	
b. chemicals added				
MgSO <sub>4</sub> ·7H <sub>2</sub> O	6.5	0.63	5.55	0.61
Silicate	25.95	2.52	44.5	4.9
NaOH	50.0	4.9	41.20	4.5
H <sub>2</sub> O <sub>2</sub>	55.0	3.3	45.22	4.9
4. Total Chemicals Added				
DPTA		0.51		0.49
HEEDTA		0.51		0.49
MgSO <sub>4</sub> ·7H <sub>2</sub> O		1.27		1.26
Silicate		5.23		4.90
NaOH		4.9		4.5
H <sub>2</sub> O <sub>2</sub>		5.3		4.9

## 5. Test Results

		CA	CA
	ISO brightness (%)	74.2	75.7
5	H <sub>2</sub> O <sub>2</sub> consumed (%)	5.03	3.65
	NaOH consumed (%)	3.68	2.88
	PUR 3rd stage (l/kg)	0.97	1.1
	Mn in chips		
	3rd stage (ppm)	31.5	29.1
	Mg in chips		
	3rd stage (ppm)	430	722
10	Mn content original		
	chips (ppm)	162.7	162.7
	Mg content original		
	chips (ppm)	110.1	110.1

COMPARISON

15	<u>Control:</u>	74.2% brightness WITH 5.03% H <sub>2</sub> O <sub>2</sub> consumption 31.53% ppm Mn in 3rd stage chips 430 ppm Mg in 3rd stage chips
	<u>Invention:</u>	75.7% brightness with 3.65% H <sub>2</sub> O <sub>2</sub> consumption 29.1% ppm Mn in 3rd stage chips 722 ppm Mg in 3rd stage chips
20	<u>Improvement:</u>	1.5 greater brightness units 2% less H <sub>2</sub> O <sub>2</sub> consumption 2.43 ppm less Mn in 3rd stage chips 292 ppm more Mg in 3rd stage chips

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EXAMPLES C (CONTROL) AND 3

30 Screened aspen (populus tremuloides) chips at a solid content of 58.2% were impregnated and refined using the general procedures described in Example A. The pH of the first stage liquor was adjusted to 7.0 and the 2nd stage liquor had a pH of 10.7. This is designated Example C. An identical aspen chip charge was impregnated and refined by the general procedures of Example 1 above using the sequence of this invention. The specific additions used and results obtained are shown in Table III.

35 Although the original aspen chips had a low manganese content resulting in a low 3rd stage manganese level in the chips in both Examples C and 3, the third stage chips of Example 3 retained much more magnesium. As a result, brightness was improved by 1.2% while peroxide consumption was reduced by about 18% vs. the control.

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TABLE III

The process conditions, added chemical amounts, test results of 3-stage alkaline peroxide process of present invention vs. control 3-stage process.

EXAMPLE NO.	C (CONTROL)		#3	
1. 1st Impregnation				
a. process conditions				
pH	7.0		11.1	
b. chemicals added	CL	CA	CL	CA
DTPA	1.45	0.24	2.6	0.37
HEEDTA	1.45	0.24	2.65	0.37
MgSO <sub>4</sub> ·7H <sub>2</sub> O	3.6	0.59	2.65	-
2. 2nd Impregnation				
a. process conditions				
pH	10.7		9.5	
b. chemicals added				
DTPA	1.55	0.25	-	-
HEEDTA	1.55	0.25	-	-
Silicate	15.4	2.53	-	-
MgSO <sub>4</sub> ·7H <sub>2</sub> O	-	-	3.55	0.55
3. 3rd Impregnation				
a. process conditions				
pH	11.6		11.8	
b. chemicals added				
MgSO <sub>4</sub> ·7H <sub>2</sub> O	4.15	0.62	4.15	0.63
Silicate	16.65	2.50	33.3	5.02
NaOH	37.5	5.63	38.8	5.86
H <sub>2</sub> O <sub>2</sub>	23.4	4.41	29.2	4.41
4. Total Chemicals Added				
DTPA		0.49		0.37
HEEDTA		0.49		0.37
MgSO <sub>4</sub> ·7H <sub>2</sub> O		1.21		1.18
Silicate		5.03		5.02
NaOH		5.63		5.86
H <sub>2</sub> O <sub>2</sub>		4.41		4.41

## 5. Test Results

	CA	CA
ISO brightness (%)	78.9	80.1
H <sub>2</sub> O <sub>2</sub> consumed (%)	3.54	2.92
NaOH consumed (%)	4.57	4.15
PUR 3rd stage (1/kg)*	1.5	1.5
Mn in chips		
3rd stage (ppm)	2.9	5.2
Mg in chips		
3rd stage (ppm)	471	746
Mn content original		
chips (ppm)	9.3	9.3
Mg content original		
chips (ppm)	137	137

COMPARISON

<u>Control:</u>	78.9% brightness 3.54% H <sub>2</sub> O <sub>2</sub> consumption 441 ppm Mg in 3rd stage chips
<u>Invention:</u>	80.1% brightness 2.92% H <sub>2</sub> O <sub>2</sub> consumption 746 ppm Mg in 3rd stage chips
<u>Improvement:</u>	Process: 1.2 greater brightness units 18% less in H <sub>2</sub> O <sub>2</sub> consumption 293 ppm more Mg in 3rd stage chips

\* See definition of PUR in Examples A and B.

EXAMPLES D - N and 4-7

A lodgepole pine/white spruce (50/50%) chips mixture was subjected to both the 3-stage process of the present invention and that of the control process used in Example A. The same general impregnation and refining conditions were employed as in the previous examples along with comparable chemical applications while the specific conditions are given in Table IV. Table IV compares the brightness values, chemical compositions and Mn and Mg content for identical chip charges and both examples D, E, F, G (control) examples with 4, 5, 6 and 7, respectively (process of invention). In all cases, brightness is higher and peroxide consumption lower for examples 4, 5, 6, and 7. Also, chips impregnated in example 4, 5, 6 and 7 always have a lower Mn content and a higher Mg content after the 3rd impregnation stage, thus leading to greater peroxide efficiency in pulp brightening.

Brightness gains attributable to the process of invention range from 1.8 to 6.2% ISO, while peroxide consumption is reduced by from 13 to 28% compared to the control.

TABLE IV

Comparative test results of 3-stage alkaline peroxide process of the present invention vs control 3-stage process.								
EXAMPLE No.	D	4	E	5	F	6	G	7
ISO Brightness	74.2	76.0	67.7	71.7	66.4	72.6	72.0	74.8
PUR (1/kg)	0.85	0.91	0.70	0.75	0.83	0.95	1.03	1.3
H <sub>2</sub> O <sub>2</sub> Consumed (%)	2.78	2.00	2.53	2.19	3.10	2.43	2.20	1.78
NaOH Consumed (%)	2.20	1.88	1.82	2.27	1.81	2.07	1.76	2.24
Mn Content in 3rd stage (ppm)	12.7	8.6	20.8	12.1	24.8	7.1	12.1	4.7
Mg Content in 3rd Stage (ppm)	377	885	515	697	462	795	296	855
Mn Content in Original Wood (ppm)	83.2	83.2	62.8	62.8	72.0	72.0	67.7	67.7
Mg Content in Original Wood (ppm)	112	112	103	103	122	122	104	104

Thus, as substantiated by the examples for both hardwoods and softwoods, the 3-stage preferred

process of the present invention increased brightness and decreased  $H_2O_2$  consumption compared to the best prior art process for high yield peroxide pretreated pulp (U.S. Patent 4,849,058).

The concept and practice of the present invention leads to two major advantages over other alkaline peroxide chip treatment processes. These are:

1. More efficient removal of heavy metal ions [(particularly) manganese (Mn)], which catalyze peroxide decompositions;
2. Maintenance of a higher concentration of magnesium ions in the chips so they can protect the peroxide from decomposition prior to, during, and following the refining process.

The best mode presently contemplated for practicing the invention is with a three stage impregnation process as exemplified in Example 1 with chemical selection, concentration of impregnation solutions and chemical quantities impregnated into the chips in the ranges demonstrated in Examples 1 through 7.

The present invention, described in its broadest concept is an improvement to peroxide treatments of wood chips prior to refining in which the concentration of metal ions within the cellular structure of the chips is reduced in a first impregnation step as shown in examples 1 through 7 and followed by alkaline peroxide impregnation with stabilizers for peroxide including magnesium ions and then mechanical pulping (refining).

### Claims

1. A high yield pulping process comprising impregnating chips with an alkaline peroxide solution containing stabilizers for peroxide followed by mechanical defibration, in which the wood chips are pretreated prior to peroxide impregnation, said pretreatment comprising:
  - (a) impregnating the chips with an impregnation solution consisting essentially of a chelating agent for metallic ions; and,
  - (b) expressing from the chips chelating agents and metallic ions.
2. A process as claimed in claim 1, wherein:
  - the chelating agent in the pretreatment impregnation solution is selected from the group consisting of diethylenetriaminepentaacetic acid (DTPA), ethylene diaminetetraacetic acid (EDTA), hydroxyethylethylenediamine triacetic acid (HEEDTA), and nitrilotriacetic acid (NTA), sodium tripolyphosphate (STPP), and phosphonic acid derivatives; and is at a concentration of chelating agent of from 0.1 gram per litre to 20 grams per litre;
  - the pretreatment impregnation results in from 0.01% to 2% chelant in the chips based upon the dry weight of the chips; and
  - at least 25% of the pretreatment impregnation solution is expressed from the chips prior to impregnating the chips with alkaline peroxide.
3. A process as claimed in claim 1 or 2, further comprising a retention time of at least 30 minutes after the impregnated chips of step (a) and prior to the expression of step b.
4. A high yield alkaline peroxide pulping process for wood chips comprising:
  - (a) impregnating the wood chips with a first impregnation solution consisting essentially of a chelating agent for metallic ions;
  - (b) expressing, at least 25% of said first impregnation solution containing metallic ions from within the chips;
  - (c) removing expressed impregnation solution from contact with the chips;
  - (d) impregnating the chips with a second impregnating solution containing magnesium salts at a concentration of from 0.5% grams per litre to 20 grams per litre to result in from 0.05% to 2% by weight magnesium in the chips calculated as  $MgSO_4 \cdot 7H_2O$  and based upon the oven dried weight of the wood chips;
  - (e) impregnating the chips with a third peroxide and having a pH from 9 to 13; and
  - (f) mechanically defiberizing the chips to produce pulp.
5. A process as claimed in claim 4, wherein steps (d) and (e) are combined into a single second impregnation step with a second impregnation solution containing peroxide and a stabilizer for peroxide and having a pH from 9 to 13 and magnesium salts at a concentration of from 0.5% grams per litre to 20 grams per litre to result in from 0.05% to 2% by weight magnesium in the chips calculated as  $MgSO_4 \cdot 7H_2O$  and based upon the oven dried weight of the wood chips.

6. A process as claimed in claim 4 or 5 wherein:

the chelating agent in the first impregnation solution is selected from the group consisting of diethylenetriaminepentaacetic acid (DTPA), ethylene diaminetetraacetic acid (EDTA), hydrox-  
yethylethylenediamine triacetic acid (HEEDTA), and nitrilotriacetic acid (NTA), sodium tripolyphosphate  
(STPP), and phosphonic acid derivatives; and is at a concentration of chelating agent of from 0.1 gram  
per litre to 20 grams per litre;

the first impregnation results in from 0.01% to 2% chelant in the chips based upon the dry weight  
of the chips; and

at least 25% of the first impregnation solution is expressed from the chips prior to impregnating the  
chips with alkaline peroxide.

7. A high yield alkaline peroxide pulping process for wood chips, comprising:

(a) impregnating the wood chips with a first impregnation solution containing a chelating agent for  
metallic ions without containing significant quantities of magnesium ions;

(b) expressing said first impregnation solution containing metallic ions from within the chips;

(c) removing expressed impregnation solution from contact with the chips;

(d) impregnating the chips with a second impregnating solution containing peroxide and a stabilizer  
for peroxide and having a pH from 9 to 13 and containing magnesium salts at a concentration of  
from 0.5% grams per litre to 20 grams per litre to result in from 0.05% to 2% by weight magnesium  
in the chips calculated as  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and based upon the oven dried weight of the wood chips;  
and

(e) mechanically defiberizing the chips to produce pulp.



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## EUROPEAN SEARCH REPORT

Application Number

EP 91 31 1614

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 194 982 (EKA AB)  * column 3, line 13 - line 16 * ---	1, 2, 4, 6, 7	D21B1/16 D21C9/10 D21C9/16
D, Y	WO-A-8 701 746 (SCOTT PAPER COMPANY)  * claims * ---	1, 2, 4, 6, 7	
A	US-A-3 251 731 (GARD, A. J.)  * column 2, line 21 - line 30 * -----	1, 2, 4, 6, 7	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			D21B D21C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 APRIL 1992	Examiner BERNARDO NORIEGA F.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document  T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... A : member of the same patent family, corresponding document			

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